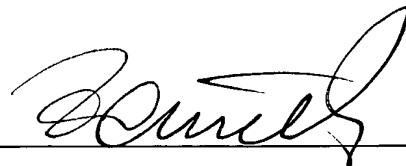


UNITED STATES PATENT AND TRADEMARK OFFICE

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4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.



For and on behalf of  
Patentanwaltskanzlei Zounek  
Translation Group

The 14th day of September 2004

Transparent, low-flammability, UV-resistant film made  
5 from a crystallizable thermoplastic, process for its  
production and its use

The invention relates to a transparent, low-flammability,  
UV-resistant, oriented film made from a crystallizable  
10 thermoplastic whose thickness is from 5 to 300 µm. The  
film comprises at least one flame retardant and one UV  
stabilizer and has good orientability and very good  
optical and mechanical properties, and can be produced  
cost-effectively. The invention further relates to the  
15 use of this film and to a process for its production.

Transparent, oriented films made from crystallizable  
thermoplastics of thickness from 1 to 300 µm are well  
known.  
20

These films comprise neither UV stabilizer as light  
stabilizer nor flame retardants. For this reason, neither  
the films nor the items produced from them are suitable  
for outdoor applications where fire protection or low  
25 flammability is a requirement. The films do not pass the  
fire tests of DIN 4102, Part 2 and Part 1, nor that of UL  
94.

In outdoor applications, even after a short period, the  
30 known films show yellowing and a deterioration in  
mechanical properties, due to photooxidative degradation  
by sunlight.

EP-A-0 620 245 describes films with improved heat  
35 resistance. These films comprise antioxidants suitable  
for scavenging free radicals formed in the film and for

degrading any peroxide formed. However, this specification makes no proposal as to how the UV resistance of films of this type may be improved.

- 5 DE-A 23 46 787 describes a low-flammability plastic. Besides the plastic, the claims also cover the use of the plastic to give films and fibers.

However, when films were produced from this phospholane-  
10 modified raw material as claimed in the DE-A publication the following shortcomings were apparent:

The plastic is very susceptible to hydrolysis and has to be very thoroughly predried. When the plastic is dried  
15 using dryers of the prior art it cakes, and if production of a film is possible at all it is possible only under very difficult conditions. The films produced under extreme, and uneconomic conditions embrittle at temperature treatment, that is to say their mechanical  
20 properties decline sharply as a result of rapid embrittlement, making the film unusable industrially. This embrittlement arises after as little as 48 hours at high temperature.

- 25 The object of the present invention was to provide a transparent, flame-retardant, UV resistant, oriented film having a thickness of from 5 to 300  $\mu\text{m}$  which can be produced cost-effectively, can readily be oriented, and has good mechanical and optical properties, and above all  
30 is flame-retardant, and does not embrittle at high temperatures and has high UV resistance.

Flame retardancy means that the transparent film complies with the conditions of DIN 4102, Part 2 and in particular  
35 the conditions of DIN 4102, Part 1 in tests known as

fire-protection tests, and can be assigned to construction materials class B2, and in particular B1, for low-flammability materials.

5 The film should also pass the UL 94 test known as the "Vertical Burning Test for Flammability of Plastic Material", so that it can be placed in class 94 VTM-0. This means that the film is no longer burning 10 seconds after removal of a Bunsen burner, and that after 30  
10 seconds there is no smouldering, and also that there is no formation of dropping of burning material during the entire period of the test.

High UV resistance means that the films suffer no damage  
15 or only extremely little damage when exposed to sunlight or other UV radiation, and therefore that the films are suitable for outdoor applications and/or critical indoor applications. In particular, when the films are used outdoors for a number of years they should in particular  
20 not yellow, nor become brittle and not have surface-cracking, and also have unimpaired mechanical properties. High UV resistance therefore implies that the film absorbs the UV light and does not transmit light until the visible region has been reached.

25 Examples of the good optical properties required are high luminous transmittance ( $\geq 84\%$ ), high surface gloss ( $\geq 120$ ), extremely low haze ( $\leq 20\%$ ), and also a low Yellowness Index ( $YID \leq 10$ ).

30 The good mechanical properties include, inter alia, a high modulus of elasticity ( $E_{MD} > 3200 \text{ N/mm}^2$ ;  $E_{TD} > 3500 \text{ N/mm}^2$ ), and also good tear strengths (in MD  $> 100 \text{ N/mm}^2$ ; in TD  $> 130 \text{ N/mm}^2$ ).

35

Good orientability includes excellent capabilities of the film for orientation during its production, both longitudinally and transversely, without break-offs.

5 Cost-effective production conditions include the capability of the plastic and of any other plastic components required for producing the low-flammability film, to be dried with industrial dryers which comply with the prior art. It is important that these raw  
10 materials do not cake or undergo thermal degradation. These industrial dryers of the prior art include vacuum dryers, fluidized-bed dryers, continuous fluidized-bed dryers, and fixed-bed dryers (tower dryers). At average they operate at temperatures of from 100 to 170°C, at  
15 which the flame-retardant plastics known hitherto cake and have to be removed by the methods used in mining, making film production impossible.

In the vacuum dryer, which has the most gentle drying  
20 action, the plastic passes through a range of temperature of from about 30 to 130°C at a pressure of 50 mbar. A process known as post drying is then required, in a hopper at temperatures of from 100 to 130°C with a residence time of from 3 to 6 hours. Even in this  
25 process, the known plastic cakes to an extreme extent.

No embrittlement on exposure to high temperature for a short period means that after 100 hours of heat treatment at 100°C in a circulating-air drying cabinet the film has  
30 not embrittled and does not have poor mechanical properties.

This object is achieved by a transparent film with a thickness of from 5 to 300 µm whose principal constituent  
35 is a crystallizable thermoplastic, wherein at least one

UV stabilizer and one flame retardant are present in the film, where according to the invention at least the flame retardant, and preferably also the UV stabilizer, is fed as a masterbatch directly into the crystallizable thermoplastic during production of the film.

The transparent film according to the invention comprises, as principal constituent, a crystallizable thermoplastic. Examples of suitable crystallizable or semicrystalline thermoplastics are polyethylene terephthalate, polybutylene terephthalate or polyethylene naphthalate, preferably polyethylene terephthalate.

For the purposes of the present invention, crystallizable thermoplastics are crystallizable homopolymers, crystallizable copolymers, crystallizable compounds, crystallizable recycled material and other types of crystallizable thermoplastics.

The novel transparent film may have either one layer or more than one layer. The film may likewise have been coated with various copolyesters or adhesion promoters.

According to the invention, the transparent film comprises, besides the crystallizable thermoplastic, a UV stabilizer and a flame retardant. According to the invention, the flame retardant is fed into the crystallizable thermoplastic directly by way of what is known as masterbatch technology during production of the film, and the concentration of flame retardant in the finished film is from 0.5 to 30% by weight, preferably from 1 to 20% by weight, based on the weight of the layer of the crystallizable thermoplastic.

It is appropriate for the UV stabilizer likewise to be

fed into the crystallizable thermoplastic directly by way of what is known as masterbatch technology during production of the film, and the concentration of the UV stabilizer in the finished film is preferably from 0.01 to 5% by weight, based on the weight of the layer of the crystallizable thermoplastic.

Light, in particular the ultraviolet content of solar radiation, i.e. the wavelength region from 280 to 400 nm, induces degradation in thermoplastics, as a result of which their visual appearance changes due to color change or yellowing, and there is also an adverse effect on mechanical/physical properties.

Inhibition of this photooxidative degradation is of considerable technical and economic importance, since otherwise there are drastic limitations on the applications of many thermoplastics.

The absorption of UV light by polyethylene terephthalates, for example, starts at below 360 nm, increases markedly below 320 nm and is very pronounced at below 300 nm. Maximum absorption occurs at between 280 and 300 nm.

In the presence of oxygen it is mainly chain cleavage which occurs, but there is no crosslinking. The predominant photooxidation products in quantity terms are carbon monoxide, carbon dioxide and carboxylic acids. Besides the direct photolysis of the ester groups, consideration has to be given to oxidation reactions which likewise form carbon dioxide, via peroxide radicals.

In the photooxidation of polyethylene terephthalate there

can also be cleavage of hydrogen at the position  $\alpha$  to the ester groups, giving hydroperoxides and decomposition products of these, and this may be accompanied by chain cleavage (H. Day, D.M. Wiles: J. Appl. Polym. Sci 16, 5 1972, p. 203).

UV stabilizers, i.e. light stabilizers which are UV absorbers, are chemical compounds which can intervene in the physical and chemical processes of light-induced degradation. Carbon black and other pigments can give 10 some protection from light. However, these substances are unsuitable for transparent films, since they cause discoloration or color change. The only compounds suitable for transparent matt films are those organic or 15 organometallic compounds which produce no, or only extremely slight, color or color change in the thermoplastic to be stabilized, that is to say they are soluble in the thermoplastic.

20 For the purposes of the present invention, UV stabilizers suitable as light stabilizers are those which absorb at least 70%, preferably 80%, particularly preferably 90%, of the UV light in the wavelength region from 180 to 380 nm, preferably from 280 to 350 nm. These are 25 particularly suitable if they are thermally stable in the temperature range from 260 to 300°C, that is to say they do not decompose and do not cause release of gases. Examples of UV stabilizers suitable as light stabilizers are 2-hydroxybenzophenones, 2-hydroxybenzotriazoles, 30 organonickel compounds, salicylic esters, cinnamic ester derivatives, resorcinol monobenzoates, oxanilides, hydroxybenzoic esters, and sterically hindered amines and triazines, and among these preference is given to the 2-hydroxybenzotriazoles and the triazines.



The UV stabilizer(s) is (are) preferably present in the outer layer(s). The core layer may also have UV stabilizer, if required.

5 It was highly surprising that the use of the abovementioned UV stabilizers in films gave the desired result. The skilled worker would probably first have attempted to achieve a certain degree of UV resistance by way of an antioxidant, but would have found that the film  
10 rapidly yellows on weathering.

In the knowledge that UV stabilizers absorb UV light and therefore provide protection, the skilled worker would be likely to have used commercially available stabilizers.  
15 He would then have observed that

- the UV stabilizer has unsatisfactory thermal stability and at temperatures of from 200 to 240°C decomposes and releases gases;
- large amounts (from about 10 to 15% by weight) of  
20 the UV stabilizer have to be incorporated so that the UV light is absorbed and the film therefore not damaged.

At these high concentrations it would have been observed  
25 that the film is already yellow just after it has been produced, with Yellowness Index deviations (YID) around 25. It would also have been observed that its mechanical properties are adversely affected. Orientation would have produced exceptional problems, such as

- 30 - break-offs due to unsatisfactory strength, i.e. modulus of elasticity too low,
- die deposits, causing profile variations,
- roller deposits from the UV stabilizer, causing impairment of optical properties (defective  
35 adhesion, nonuniform surface);

- deposits in stretching frames or heat-setting frames, dropping onto the film.

It was therefore more than surprising that even low concentrations of the UV stabilizer achieve excellent UV protection. It was very surprising that, together with this excellent UV protection:

- within the accuracy of measurement, the Yellowness Index of the film is unchanged from that of an unstabilized film;
- there are no releases of gases, no die deposits and no frame condensation, and the film therefore has excellent optical properties and excellent profile and layflat;
- the UV-stabilized film has excellent stretchability, and can therefore be produced in a reliable and stable manner on high-speed film lines at speeds of up to 420 m/min.

The film according to the invention comprises at least one flame retardant, which is fed by way of what is known as masterbatch technology directly during production of the film, and the amount of flame retardant here is from 0.5 to 30.0% by weight, preferably from 1.0 to 20.0% by weight, based on the weight of the layer of the crystallizable thermoplastic. The ratio of flame retardant to thermoplastic is generally kept at from 60:40 to 10:90% by weight during preparation of the masterbatch.

Typical flame retardants include bromine compounds, chloroparaffins and other chlorine compounds, antimony trioxide, alumina trihydrates, but the use of the halogen compounds here is disadvantageous due to the occurrence of halogen-containing byproducts. The low light

resistance of films provided with these materials is moreover a great disadvantage, as is the evolution of hydrogen halides in the event of a fire.

5 Examples of suitable flame retardants used according to the invention are organic phosphorus compounds, such as carboxyphosphinic acids, anhydrides of these and dimethyl methylphosphonate. A substantive factor according to the invention is that the organic phosphorus compound is  
10 soluble in the thermoplastic, since otherwise the optical properties required are not complied with.

Since the flame retardants generally have some susceptibility to hydrolysis, the additional use of a  
15 hydrolysis stabilizer may be desirable.

The hydrolysis stabilizers used are generally amounts of from 0.01 to 1.0% by weight of phenolic stabilizers, the alkali metal/alkaline earth metal stearates and/or the  
20 alkali metal/alkaline earth metal carbonates. The amounts of phenolic stabilizers used are preferably from 0.05 to 0.6% by weight, in particular from 0.15 to 0.3% by weight, and their molar mass is preferably above 500 g/mol. Particularly advantageous compounds are  
25 pentaerythrityl tetrakis-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate or 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene.

It was more than surprising, therefore, that by using  
30 masterbatch technology a suitable predrying and/or precrystallization procedure and, if desired, using small amounts of a hydrolysis stabilizer, it is possible to produce a low-flammability, thermoformable film with the required property profile in a cost-effective manner and  
35 without any caking in the dryer, and that on exposure to

high temperature the film does not become brittle, and does not break when folded.

It was very surprising that, together with this excellent  
5 result and with the flame retardancy required and with the high UV resistance:

- within the accuracy of measurement, there is no adverse effect on the Yellowness Index of the film, compared with that of an unmodified film;
- 10 - there are no releases of gases, no die deposits and no frame condensation, and the film therefore has excellent optical properties and excellent profile and layflat, and
- the low-flammability UV-stabilized film has  
15 excellent stretchability, and can therefore be produced in a reliable and stable manner on high-speed film lines at speeds of up to 420 m/min.

The film is therefore also cost-effective.

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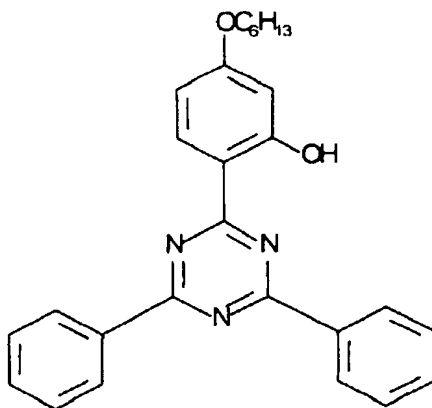
It was also very surprising that the cut film material can moreover be reused as regrind for production of the film without any adverse effect on the Yellowness Index of the film.

25

In one preferred embodiment, the transparent, low-flammability film according to the invention comprises a crystallizable polyethylene terephthalate as principal constituent, as flame retardant from 1 to 20% by weight  
30 of an organic phosphorus compound soluble in the polyethylene terephthalate, and from 0.1 to 1.0% by weight of a hydrolysis stabilizer, and from 0.01 to 5.0% by weight of a PET-soluble UV absorber selected from the group consisting of the 2-hydroxybenzotriazoles and the  
35 triazines.

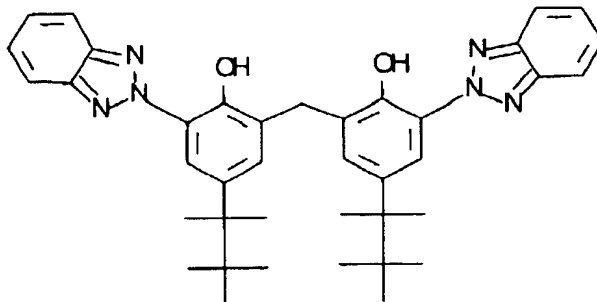
In its particularly preferred embodiment, the film according to the invention also comprises from 0.01 to 5.0% by weight of 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyl)oxyphenol of the formula:

5



or from 0.01 to 5.0% by weight of 2,2-methylenebis(6-(2H-benzotriazol-2-yl)-4-(1,1,2,2-tetramethylpropyl)phenol of the formula:

10



In one preferred embodiment it is also possible for mixtures of the two UV stabilizers mentioned or mixtures of at least one of the two UV stabilizers with other UV stabilizers to be used, where the total concentration of  
5 light stabilizer is preferably from 0.01 to 5.0% by weight, based on the weight of crystallizable polyethylene terephthalate.

The transparent, UV-resistant, low-flammability film has  
10 the following property profile:

The surface gloss, measured to DIN 67530 (measurement angle: 20°), is above 100, preferably above 120, the luminous transmittance L, measured to ASTM D 1003, is  
15 above 80%, preferably above 82%, and the haze of the film, measured to ASTM S 1003, is below 20%, preferably below 15%. These are surprisingly good properties for the UV resistance achieved in combination with the low flammability.

20

The standard viscosity SV (DCA) of the polyethylene terephthalate, measured in dichloroacetic acid to DIN 53728, is from 600 to 1000, preferably from 700 to 900.

25 The transparent polyethylene terephthalate film according to the invention which comprises at least one UV stabilizer and one flame retardant may have one layer or else more than one layer.

30 In the embodiment having more than one layer, the film has a structure of at least one core layer and at least one outer layer, and particular preference is given here to a three-layer structure of type A-B-A or A-B-C.

35 A substantive factor for this embodiment is that the

polyethylene terephthalate of the core layer has a standard viscosity similar to that of the polyethylene terephthalate of the outer layer(s) which is (are) adjacent to the core layer.

5

In one particular embodiment, the outer layers may also be composed of a polyethylene naphthalate homopolymer or of an ethylene terephthalate-ethylene naphthalate copolymer, or of a compound.

10

In this embodiment, the thermoplastics of the outer layers likewise have a standard viscosity similar to that of the polyethylene terephthalate of the core layer. In the embodiment having more than one layer, the UV stabilizer is preferably present in the outer layers. The

15

core layer may also have UV stabilizer, if required.

In the embodiment having more than one layer, the flame retardant is preferably present in the core layer, however, the outer layers may also have flame retardant, if required.

20

In another embodiment, flame retardants and UV stabilizer may also be present in the outer layers. If required and if fire-protection requirements are high, the core layer may additionally comprise what is known as a "base-level" flame retardant.

25

Unlike in the single-layer embodiment, the amounts given in % by weight for the concentrations of flame retardant and of UV stabilizer are based on the weight of the layer provided with the agents.

30

Very surprisingly, weathering tests to the test specification of ISO 4892 using the Atlas C165 Weather-

35

Ometer showed that in the case of a three-layer film the provision of UV stabilizers in the outer layers of from 0.5 to 2  $\mu$ m in thickness is fully sufficient to improve UV resistance.

5

Again surprisingly, fire tests to DIN 4102 Part 1 and Part 2, and also the UL 94 test, have shown that films according to the invention fulfill the requirements.

10 The low-flammability, UV-stabilized films having more than one layer and produced by known coextrusion technology are therefore of major interest in economic terms when compared with fully UV-stabilized and flame-retardant monofilms, since markedly less additives are  
15 needed to achieve comparable low flammability and UV stability.

There may also be provision, on at least one side of the film, of a scratch-resistant coating, a copolyester or an  
20 adhesion promoter.

Weathering tests have shown that, even after from 5 to 7 years in an outdoor application (extrapolated from the specific weathering tests), the low-flammability, UV-  
25 stabilized films according to the invention generally show no increase in yellowing, no embrittlement, no loss of surface gloss, no surface cracking and no impairment of mechanical properties.

30 During production of the film it was found that the low-flammability, UV-stabilized film can readily be oriented longitudinally and transversely without break-offs. In addition, no releases of gases of any type were found during the production process, and this is attributable  
35 to the presence of the UV stabilizer or the flame



retardant. This is a substantive factor for the invention, since most conventional UV stabilizers and flame retardants evolve very undesirable and unpleasant gases, attributable to the decomposition of these compounds under the conditions of processing, at extrusion temperatures above 260°C, and are therefore of no use.

Surprisingly, even films according to the invention in the thickness range from 5 to 300 µm comply with requirements for the construction materials class B1 to DIN 4102 Part 1 and with those for the UL 94 test.

During the production of the low-flammability, UV-resistant film it was also found that the flame retardant can be incorporated using masterbatch technology and suitable predrying or precrystallization respectively of the flame retardant masterbatch, without caking occurring in the dryer, and cost-effective production of the film is therefore possible.

It was more than surprising that the incorporation is made even easier by small additions of a hydrolysis stabilizer in the flame retardant masterbatch. The throughputs, and thus the production rates, could therefore be increased without difficulty. In a very specific embodiment, the film also comprises small amounts of a hydrolysis stabilizer in the layers which have flame retardant.

Measurements showed that the film according to the invention does not become brittle over a long period at high temperatures of 100°C, a fact which is more than surprising. This result is attributable to the synergistic action of suitable precrystallization,

predrying, masterbatch technology and provision of UV stabilizer.

5 The film according to the invention can moreover readily be recycled without pollution of the environment and without loss of mechanical properties, and examples of uses for which it is suitable are therefore short-lived promotional placards for constructing exhibition stands and other promotional requisites where fire protection is  
10 desirable.

An example of a production method for the transparent, low-flammability, UV-resistant film according to the invention is extrusion on an extrusion line.

15 According to the invention, the flame retardant, with or without the hydrolysis stabilizer, is fed by way of masterbatch technology. The flame retardant is fully dispersed in a carrier material. Carrier materials which  
20 may be used are the thermoplastic itself, e.g. the polyethylene terephthalate, or else other polymers compatible with the thermoplastic.

25 According to the invention, the UV stabilizer may be added at an early stage during production of the thermoplastic polymer, or fed into the extruder during production of the film.

30 It is particularly preferable for the UV stabilizer to be added by way of masterbatch technology. The UV stabilizer is fully dispersed in a solid carrier material. Carrier materials which may be used are certain resins, the thermoplastic itself, e.g. the polyethylene terephthalate, or else other polymers sufficiently  
35 compatible with the thermoplastic.

It is important in masterbatch technology that the particle size and the bulk density of the masterbatch similar to the particle size and the bulk density of the thermoplastic, so that homogeneous distribution is achieved, and with this uniform UV stabilization can be achieved.

The polyester films may be produced by known processes from a polyester raw material with, if desired, other raw materials, with the flame retardant, with the hydrolysis stabilizer if used, with the UV stabilizer and/or with other customary additives in customary amounts of from 1.0 to a maximum of 30% by weight, either in the form of a monofilm or else in the form of, if desired coextruded, films having more than one layer and with identical or differently constructed surfaces, where one surface may, for example, have been pigmented but no pigment is present at the other surface. Known processes may also have been used to provide one or both surfaces of the film with a conventional functional coating.

A substantive factor for the invention is that the masterbatch which comprises the flame retardant and, if used, the hydrolysis stabilizer, is precrystallized or predried respectively. This predrying includes gradual heating of the masterbatch at reduced pressure (from 20 to 80 mbar, preferably from 30 to 60 mbar, in particular from 40 to 50 mbar), with agitation, and, if desired, post-drying at a constant, elevated temperature, again at reduced pressure. It is preferable for the masterbatch to be charged at room temperature from a metering vessel in the desired blend together with the polymer of the base and/or outer layers and, if desired, with other raw material components batchwise into a vacuum dryer in which the temperature profile moves from 10 to 160°C,

preferably from 20 to 150°C, in particular from 30 to 130°C, during the course of the drying time or residence time. During the residence time of about 6 hours, preferably 5 hours, in particular 4 hours, the raw material mixture is stirred at from 10 to 70 rpm, preferably from 15 to 65 rpm, in particular from 20 to 60 rpm. The resultant precrystallized or predried respectively raw material mixture is post-dried in a downstream vessel, likewise evacuated, at temperatures of from 90 to 180°C, preferably from 100 to 170°C, in particular from 110 to 160°C, for from 2 to 8 hours, preferably from 3 to 7 hours, in particular from 4 to 6 hours.

In the preferred extrusion process for producing the polyester film, the molten polyester material is extruded through a slot die and quenched on a chill roll, in the form of a substantially amorphous prefilm. This amorphous prefilm is then reheated and stretched longitudinally and transversely, or transversely and longitudinally, or longitudinally, transversely and again longitudinally and/or transversely. In general, the stretching temperatures are from  $T_g + 10^\circ\text{C}$  to  $T_g + 60^\circ\text{C}$  (where  $T_g$  is the glass transition temperature), the longitudinal stretching ratio is usually from 2 to 6, in particular from 3 to 4.5, and the transverse stretching ratio is from 2 to 5, in particular from 3 to 4.5, and the ratio for any second longitudinal or transverse stretching carried out is from 1.1 to 5. The first longitudinal stretching may, if desired, be carried out simultaneously with the transverse stretching (simultaneous stretching). This is followed by the heat-setting of the film at oven temperatures of from 180 to 260°C, in particular from 220 to 250°C. The film is then cooled and wound up.

The surprising combination of excellent properties makes the film according to the invention highly suitable for a variety of different applications, such as interior decoration, for constructing exhibition stands, for  
5 exhibition requisites, for displays, for placards, for protective glazing of machines or vehicles, in the lighting sector, in fitting out shops or stores, or as a promotional requisite or laminating material, for  
10 greenhouses, roofing systems, exterior cladding, protective coverings, applications in the construction sector and illuminated advertizing profiles or blinds or electrical applications.

The examples below illustrate the invention in more  
15 detail.

The following standards and methods are used here when testing individual properties.

## 20 **Test methods**

### **Surface gloss**

Surface gloss is measured with a measurement angle of 20° to DIN 67530.

25

### **Luminous transmittance**

Luminous transmittance is the ratio of total light transmitted to the amount of incident light.

30 Luminous transmittance is measured using "®HAZEGARD plus" apparatus to ASTM D 1003.

### **Haze**

Haze is that percentage proportion of the transmitted  
35 light which deviates by more than 2.5° from the average

direction of the incident light beam. Clarity is determined at an angle of less than 2.5°.

The haze is measured using "HAZEGARD plus" apparatus to  
5 ASTM D 1003.

#### **Surface defects**

Surface defects are determined visually.

#### 10 **Mechanical properties**

The modulus of elasticity, tear strength and elongation at break are measured longitudinally and transversely to ISO 527-1-2.

#### 15 **SV (DCA), IV (DCA)**

The standard viscosity SV (DCA) is measured by a method based on DIN 53726 in dichloroacetic acid.

The intrinsic viscosity (IV) is calculated as follows  
20 from the standard viscosity

$$IV (DCA) = 6.67 \cdot 10^{-4} SV (DCA) + 0.118$$

#### **Fire performance**

Fire performance is determined to DIN 4102, Part 2,  
25 construction materials class B2, and to DIN 4102, Part 1, construction materials class B1, and also by the UL 94 test.

#### **Weathering (on both sides), UV resistance**

30 UV resistance is tested as follows to the test specification of ISO 4892

Test equipment : Atlas Ci 65 Weather-Ometer

Test conditions : ISO 4892, i.e. artificial  
35 weathering

Irradiation time : 1000 hours (per side)  
Irradiation : 0.5 W/m<sup>2</sup>, 340 nm  
Temperature : 63°C  
Relative humidity : 50%  
5 Xenon lamp : Internal and external filter  
made from borosilicate  
Irradiation cycles : 102 minutes of UV light, then  
18 minutes of UV light with  
water spray onto the specimens,  
10 then another 102 minutes of UV  
light, etc.

Numerical values of < 0.3 are negligible and indicate  
that there is no significant color change.

15

#### **Yellowness Index**

The Yellowness Index (YID) is the deviation from the  
colorless condition in the "yellow" direction and is  
measured to DIN 6167. Yellowness Index values (YID) < 5  
20 are not visible.

In the examples and comparative examples below each of  
the films is a transparent film of different thickness,  
produced on the extrusion line described.

25

Each of the films was first weathered to the test  
specification of ISO 4892 for 1000 hours per side, using  
an Atlas Ci 65 Weather-Ometer from Atlas, and then tested  
for mechanical properties, Yellowness Index (YID),  
30 surface defects, luminous transmittance and gloss.

The fire tests to DIN 4102, Part 2 and Part 1, and the UL  
94 test, were carried out on each film.

35 **Examples**

**Example 1**

A transparent film of 50  $\mu\text{m}$  thickness is produced, comprising polyethylene terephthalate as principal constituent, 0.2% by weight of <sup>®</sup>Sylobloc as antiblocking agent, 4% by weight of the organic phosphorus compound as flame retardant and 1.0% by weight of the UV stabilizer 2-(4,6-diphenyl-1,3,5-triazin-2yl)-5-(hexyl)oxyphenol (<sup>®</sup>Tinuvin 1577).

To obtain homogeneous distribution, 0.2% by weight of Sylobloc is incorporated directly into the polyethylene terephthalate (PET) when the polymer is prepared.

The polyethylene terephthalate from which the transparent film is produced has a standard viscosity SV (DCA) of 810, corresponding to an intrinsic viscosity IV (DCA) of 0.658 dl/g.

Tinuvin 1577 has a melting point of 149°C and is thermally stable up to about 330°C. The UV stabilizer Tinuvin 1577 is fed in the form of a masterbatch. The masterbatch is composed of 5% by weight of Tinuvin 1577 as active ingredient and 95% by weight of PET having a standard viscosity SV (DCA) = 810, corresponding to an intrinsic viscosity IV (DCA) of 0.658 dl/g.

The flame retardant is the organic phosphorus compound dimethyl methylphosphonate, <sup>®</sup>Amgard P 1045 from Albright & Wilson, which is soluble in PET.

The flame retardant is likewise fed in the form of a masterbatch. The masterbatch is composed of 20% by weight of flame retardant and 80% by weight of PET having a standard viscosity SV (DCA) of 810.



Both of the masterbatches have a bulk density of 750 kg/m<sup>3</sup>.

40% by weight of PET with 0.2% by weight of Sylobloc, 30%  
 5 by weight of recycled PET material, 10% by weight of UV  
 masterbatch and 20% by weight of flame retardant  
 masterbatch are discharged at room temperature from  
 separate metering vessels into a vacuum dryer which  
 operates with a temperature profile of from 25 to 130°C  
 10 from the time of charging to the end of the residence  
 time. During the residence time of about 4 hours, the  
 mixture of raw materials is agitated at 61 rpm.

The precrystallized or predried respectively mixture of  
 15 raw materials is post-dried for 4 hours at 140°C in a  
 downstream hopper, again in vacuo.

The 50 µm monofilm is then produced by the extrusion  
 process described.

20

The transparent PET film produced has the following  
 property profile:

	Thickness	:	50 µm
25	Surface gloss, Side 1	:	155
	(Measurement angle 20°) Side 2	:	152
	Luminous transmittance	:	91%
	Haze	:	4.0%
	Surface defects per m <sup>2</sup>	:	none
30	(cracks, embrittlement)		
	Longitudinal modulus of elasticity	:	4100 N/mm <sup>2</sup>
	Transverse modulus of elasticity	:	5400 N/mm <sup>2</sup>
	Longitudinal tear strength	:	170 N/mm <sup>2</sup>
	Transverse tear strength	:	260 N/mm <sup>2</sup>
35	Yellowness Index (YID)	:	3.1

After 200 hours of heat treatment at 100°C in a circulating-air drying cabinet there is no change in mechanical properties. The film shows no embrittlement phenomena of any kind.

5

The film complies with the requirements for construction material classes B2 and B1 to DIN 4102 Part 2/Part 1. The film passes the UL 94 test.

10 After in each case 1000 hours of weathering per side with the Atlas Ci 65 Weather-Ometer, the PET film has the following properties:

	Thickness	:	50 μm	
15	Surface gloss,	Side 1	:	148
	(Measurement angle 20°)	Side 2	:	146
	Luminous transmittance	:	89.9%	
	Haze	:	4.2%	
	Surface defects per m <sup>2</sup>	:	none	
20	(cracks, embrittlement)			
	Longitudinal modulus of elasticity	:	3950 N/mm <sup>2</sup>	
	Transverse modulus of elasticity	:	5200 N/mm <sup>2</sup>	
	Longitudinal tear strength	:	151 N/mm <sup>2</sup>	
	Transverse tear strength	:	238 N/mm <sup>2</sup>	
25	Yellowness Index (YID)	:	3.1	

### Example 2

Coextrusion technology is used to produce a multilayer PET film having the layer sequence A-B-A and a thickness  
30 of 17 µm, B being the core layer and A being the outer layers. The core layer has a thickness of 15 µm, and each of the two outer layers, which cover the core layer, has a thickness of 1 µm.

35 The polyethylene terephthalate used for the core layer B

is identical with the polymer of Example 1 except that it comprises no Sylobloc. The core layer comprises 0.2% by weight of hydrolysis stabilizer and 5% by weight of flame retardant. As in Example 1, the hydrolysis stabilizer and the flame retardant are fed in the form of a masterbatch. The masterbatch is composed of 25% by weight of flame retardant, 1% by weight of hydrolysis stabilizer and 74% by weight of polyethylene terephthalate. The hydrolysis stabilizer and the flame retardant are identical with the active ingredients used in Example 1.

The polyethylene terephthalate of the outer layers A is identical with the polyethylene terephthalate of Example 1, that is to say the outer layer raw material has 0.2% by weight of Sylobloc. The outer layers comprise no hydrolysis stabilizer and no flame retardant. The outer layers additionally comprise 1.0% by weight of Tinuvin 1577, and this amount was incorporated directly when the raw material was prepared.

For the core layer, 50% by weight of polyethylene terephthalate, 30% by weight of recycled polyethylene terephthalate material and 20% by weight of the masterbatch were precrystallized, predried and post-dried as in Example 1.

The outer layer raw material, which comprises Sylobloc and 1% by weight of Tinuvin 1577, is not subjected to any particular drying. Coextrusion technology is used to produce a film having the layer sequence A-B-A and having a thickness of 17  $\mu\text{m}$  and the following property profile:

Layer structure	:	A-B-A
Thickness	:	17 $\mu\text{m}$
Surface gloss, Side 1	:	174

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	(Measurement angle 20°)	Side 2	:	169
	Luminous transmittance		:	94.2%
	Haze		:	2.1%
	Surface defects per m <sup>2</sup>		:	none
5	(cracks, embrittlement)			
	Longitudinal modulus of elasticity		:	4100 N/mm <sup>2</sup>
	Transverse modulus of elasticity		:	4720 N/mm <sup>2</sup>
	Longitudinal tear strength		:	180 N/mm <sup>2</sup>
	Transverse tear strength		:	205 N/mm <sup>2</sup>
10	Yellowness Index (YID)		:	2.9

After 200 hours of heat treatment at 100°C in a circulating-air drying cabinet there is no change in mechanical properties. The film shows no embrittlement phenomena of any kind.

The film complies with the requirements for construction material classes B2 and B1 to DIN 4102 Part 2 and Part 1. The film passes the UL test.

20

After in each case 1000 hours of weathering per side with the Atlas Ci 65 Weather-Ometer the PET film has the following properties:

25	Thickness		:	17 µm
	Surface gloss,	Side 1	:	168
	(Measurement angle 20°)	Side 2	:	160
	Luminous transmittance		:	91.6%
	Haze		:	2.9%
30	Surface defects per m <sup>2</sup>		:	none
	(cracks, embrittlement)			
	Longitudinal modulus of elasticity		:	3800 N/mm <sup>2</sup>
	Transverse modulus of elasticity		:	4450 N/mm <sup>2</sup>
	Longitudinal tear strength		:	150 N/mm <sup>2</sup>
35	Transverse tear strength		:	170 N/mm <sup>2</sup>

Yellowness Index (YID) : 3.5

**Example 3**

As in Example 2, an A-B-A film of 20  $\mu\text{m}$  thickness is  
5 produced, the core layer B having a thickness of 16  $\mu\text{m}$   
and each outer layer A having a thickness of 2  $\mu\text{m}$ .

The core layer B comprises only 5% by weight of the flame  
retardant masterbatch of Example 2.

10

The outer layers are identical with those of Example 2,  
except that they additionally comprise 20% by weight of  
the flame retardant masterbatch, used in Example 2 only  
for the core layer.

15

The raw materials and the masterbatches for the core  
layer and the outer layers are precrystallized, predried  
and post-dried as in Example 1. The multilayer 20  $\mu\text{m}$  film  
produced using coextrusion technology has the following  
20 property profile:

Layer structure	:	A-B-A
Thickness	:	20 $\mu\text{m}$
Surface gloss,	Side 1	: 168
25 (Measurement angle 20°)	Side 2	: 163
Luminous transmittance	:	94.0%
Haze	:	2.2%
Surface defects per $\text{m}^2$ (cracks, embrittlement)	:	none
30 Longitudinal modulus of elasticity	:	4000 $\text{N/mm}^2$
Transverse modulus of elasticity	:	4700 $\text{N/mm}^2$
Longitudinal tear strength	:	180 $\text{N/mm}^2$
Transverse tear strength	:	205 $\text{N/mm}^2$
Yellowness Index (YID)	:	2.9

35

After 200 hours of heat treatment at 100°C in a circulating-air drying cabinet there is no change in mechanical properties. The film shows no embrittlement phenomena of any kind.

5

The film complies with the requirements for the construction material classes B2 and B1 to DIN 4102 Part 2 and Part 1. The film passes the UL test.

10 After in each case 1000 hours of weathering per side with the Atlas Ci 65 Weather-Ometer the PET film has the following properties:

	Thickness	:	20 μm	
15	Surface gloss,	Side 1	:	161
	(Measurement angle 20°)	Side 2	:	155
	Luminous transmittance	:	91.2%	
	Haze	:	3.1%	
	Surface defects per m <sup>2</sup>	:	none	
20	(cracks, embrittlement)			
	Longitudinal modulus of elasticity	:	3750 N/mm <sup>2</sup>	
	Transverse modulus of elasticity	:	4400 N/mm <sup>2</sup>	
	Longitudinal tear strength	:	150 N/mm <sup>2</sup>	
	Transverse tear strength	:	165 N/mm <sup>2</sup>	
25	Yellowness Index (YID)	:	3.6	

#### Comparative Example 1

Example 2 is repeated, except that the film is not provided with UV stabilizers, nor with flame retardant masterbatch, that is to say the film comprises no hydrolysis stabilizer, no flame retardant and no UV stabilizer.

35 The property profile of the film without these additives is comparable with that of the film of Example 2, which

has these additives.

The film without these additives does not pass the tests to DIN 4102, Part 1 and Part 2, or the UL 94 test.

5

After 1000 hours of weathering per side with the Atlas Ci Weather-Ometer, the film shows surface cracking and embrittlement phenomena. It is therefore no longer possible to measure a precise property profile - in particular to measure mechanical properties. The film is also visibly yellow.

10

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Patent claims

- 5     1.    A transparent, low-flammability, UV-resistant, oriented film made from a crystallizable thermoplastic and having a thickness of from 5 to 300  $\mu$ m, wherein the film comprises at least one UV stabilizer and at least one flame retardant, where  
10     at least the flame retardant, and preferably also the UV stabilizer, is fed directly as a masterbatch to the crystallizable thermoplastic during production of the film.
- 15     2.    The film as claimed in claim 1, wherein the crystallizable thermoplastic present comprises polyethylene terephthalate, polybutylene terephthalate or polyethylene naphthalate, preferably polyethylene terephthalate.
- 20     3.    The film as claimed in claim 1 or 2, which has one or more layers and has additionally been coated with copolyesters or with adhesion promoters.
- 25     4.    The film as claimed in any one of claims 1 to 3, wherein the amount of flame retardant present is from 0.5 to 30% by weight, preferably from 1 to 20% by weight, based on the weight of the layer of the crystallizable thermoplastic.
- 30     5.    The film as claimed in any one of claims 1 to 4, wherein the amount of the UV stabilizer present is from 0.01 to 5% by weight, based on the weight of the layer of the crystallizable thermoplastic.



6. The film as claimed in any one of claims 1 to 5,  
wherein the UV stabilizers present comprise light  
stabilizers selected from the group consisting of  
the 2-hydroxybenzophenones, 2-hydroxybenzotriazoles,  
organonickel compounds, salicylic esters, cinnamic  
ester derivatives, resorcinol monobenzoates,  
oxanilides, hydroxybenzoic esters, sterically  
hindered amines and triazines, and preference is  
given to the 2-hydroxybenzotriazoles and the  
triazines.
7. The film as claimed in any one of claims 1 to 6,  
wherein the flame retardants present comprise  
organic phosphorus compounds, in particular organic  
phosphorus compounds soluble in polyethylene  
terephthalate.
8. The film as claimed in claim 7, wherein the flame  
retardant present comprises the bisglycol ester of  
2-carboxyethyl-methyl phosphinic acid or of the  
cyclic anhydride 2-methyl-2,5-dioxo-1,2-oxophos-  
pholane, respectively.
9. The film as claimed in any one of claims 1 to 8,  
wherein from 0.1 to 1.0% by weight of a hydrolysis  
stabilizer selected from the group consisting of  
alkali metal/alkaline earth metal stearates and/or  
alkali metal/alkaline earth metal carbonates, or  
from 0.05 to 0.6% by weight, in particular from 0.1  
to 0.3% by weight, of a hydrolysis stabilizer  
selected from the group consisting of the phenolic  
stabilizers having a molar mass above 500 g/mol, in  
particular pentaerythrityl tetrakis-3-(3,5-di-tert-  
butyl-4-hydroxyphenyl)propionate or 1,3,5-trimethyl-  
2,4,6-tris(3,5-di-tert-butyl-4-hydroxy-

benzyl)benzene, is additionally present in the film.

10. The film as claimed in any one of claims 1 to 9,  
wherein the organic phosphorus compounds present in  
5 the film comprise long-chain, encapsulated ammonium  
polyphosphates or carboxyphosphinic acids or  
anhydrides of these and, besides the hydrolysis  
stabilizer, from 0.01 to 5.0% by weight of 2-(4,6-  
diphenyl-1,3,5-triazin-2-yl)-5-(hexyl)oxyphenol or  
10 from 0.01 to 5.0% by weight of 2,2-methylenebis(6-  
(2H-benzotriazol-2-yl)-4-(1,1,2,2-  
tetramethylpropyl)phenol or mixtures of these UV  
stabilizers or mixtures of at least one of these two  
UV stabilizers with other UV stabilizers are present  
15 in the film, where the total amount of UV stabilizer  
is from 0.01 to 5.0% by weight, based on the weight  
of crystallizable polyethylene terephthalate.
11. The film as claimed in any one of claims 1 to 10,  
20 wherein the surface gloss of the film, measured to  
DIN 67530 (measurement angle: 20°), is above 100,  
preferably above 120, and wherein its luminous  
transmittance L, measured to ASTM D 1003, is above  
80%, preferably above 82%, and wherein its haze,  
25 measured to ASTM S 1003, is below 20%, preferably  
below 15%.
12. A process for producing a transparent, low-  
flammability, UV-resistant film as claimed in any  
30 one of claims 1 to 11 by extrusion on an extrusion  
line, which comprises adding the flame retardant, if  
desired together with the hydrolysis stabilizer, by  
way of masterbatch technology, where the flame  
retardant has been fully dispersed in a solid  
35 carrier material, for example in the thermoplastic

itself, in polyethylene terephthalate or in another polymer compatible with the thermoplastic.

13. The process as claimed in claim 12, wherein the UV  
5 stabilizer, too, is added by way of masterbatch  
technology, where the UV stabilizer has been fully  
dispersed in a solid carrier material, for example  
in resin, in the thermoplastic itself, in  
polyethylene terephthalate or in another polymer  
10 sufficiently compatible with the thermoplastic.
14. The process as claimed in claim 12 or 13, wherein  
the particle size and the bulk density of the  
masterbatch are set to be similar to the particle  
15 size and the bulk density of the thermoplastic.
15. The process as claimed in any one of claims 12 to  
14, wherein the masterbatch in which the flame  
retardant and the hydrolysis stabilizer are present  
20 is precrystallized or predried respectively, by  
taking the masterbatch at room temperature from a  
metering vessel in the desired blend together with  
the thermoplastic and, if desired, with other raw  
material components, batchwise into a vacuum dryer  
25 which then operates with a temperature profile of  
from 20 to 130°C during the course of the drying  
time or residence time, and during the residence  
time of from 2 to 4 hours the mixture of raw  
materials is stirred at from 10 to 70 rpm.  
30
16. The process as claimed in any one of claims 12 to  
15, wherein the precrystallized or predried  
respectively mixture of raw materials is post-dried  
in a downstream vessel, likewise evacuated, at a  
35 temperature of from 100 to 170°C.

17. The use of a film as claimed in any one of claims 1 to 11, produced by a process of any one of claims 12 to 16, for interior decoration, for constructing exhibition stands, for exhibition requisites, as a display, for placards, for protective glazing of machines or of vehicles, in the lighting sector, for the fitting out of shops or stores, as a promotional requisite, as a laminating medium, for greenhouses, for roofing systems, for exterior cladding, for protective coverings and for applications in the construction sector, such as illuminated advertizing profiles, blinds or electrical applications.

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Abstract

Transparent, low-flammability, UV-resistant film made  
from a crystallizable thermoplastic, process for its  
5 production and its use

The present invention relates to a transparent, low-  
flammability, UV-resistant, oriented film made from a  
crystallizable thermoplastic and having a thickness of  
10 from 5 to 300  $\mu\text{m}$ . The film comprises at least one UV  
stabilizer and at least one flame retardant, and at least  
the flame retardant, and preferably also the UV  
stabilizer, is fed directly as a masterbatch to the  
crystallizable thermoplastic during production of the  
15 film. The film may have one or more layers, and the UV  
stabilizer may have been selected from the group  
consisting of the 2-hydroxybenzophenones, the  
2-hydroxybenzotriazoles, the organonickel compounds, the  
salicylic esters, the cinnamic ester derivatives, the  
20 resorcinol monobenzoates, the oxanilides, the  
hydroxybenzoic esters, the sterically hindered amines and  
triazines, and the flame retardant may be an organic  
phosphorus compound, in particular an organic phosphorus  
compound soluble in polyethylene terephthalate.